UNLOCKING the potential of LOHCs through the development of KEy sustainable and efficient systems for Dehydrogenation HORIZON-JTI-CLEANH2-2022-02-05

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IRCELYON - CP2M



Ircelyon

INSTITUT DE RECHERCHES SUR LA CATALYSE ET L'ENVIRONNEMENT May 2023





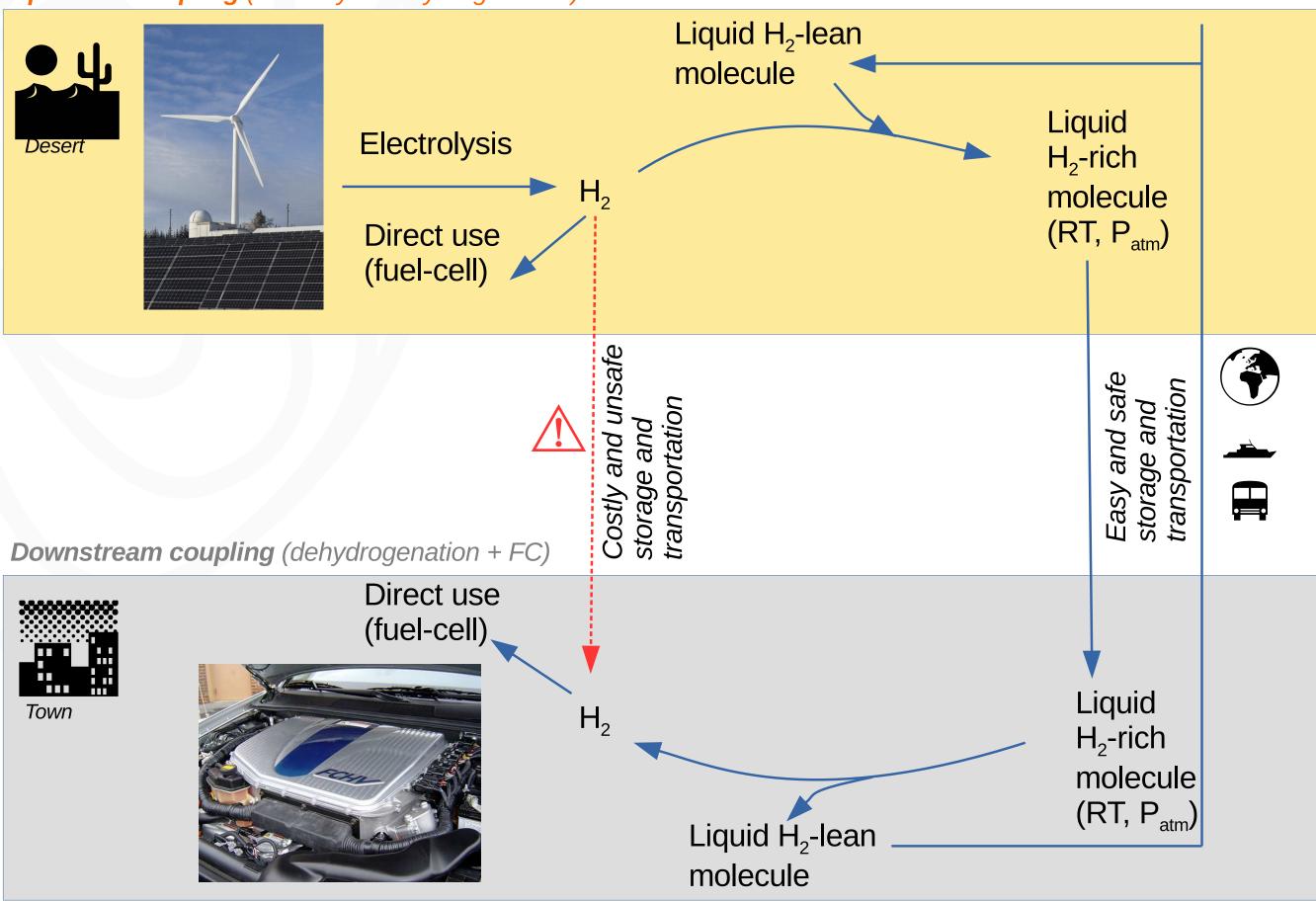


Context of LOHC

Context of LOHC

The project Methodology Tasks Dehydrogenation issues Dehydrogenation reactor Liquid phase analysis HO-BT/H12-BT pair Catalysts Bimetallic catalysts Single-atom catalysts... ...or nano-clusters Hsp supports for hydrogenation Hsp supports for dehydrogenation Conclusion ICC 2024

Upstream coupling (electrolysis + hydrogenation)





The project

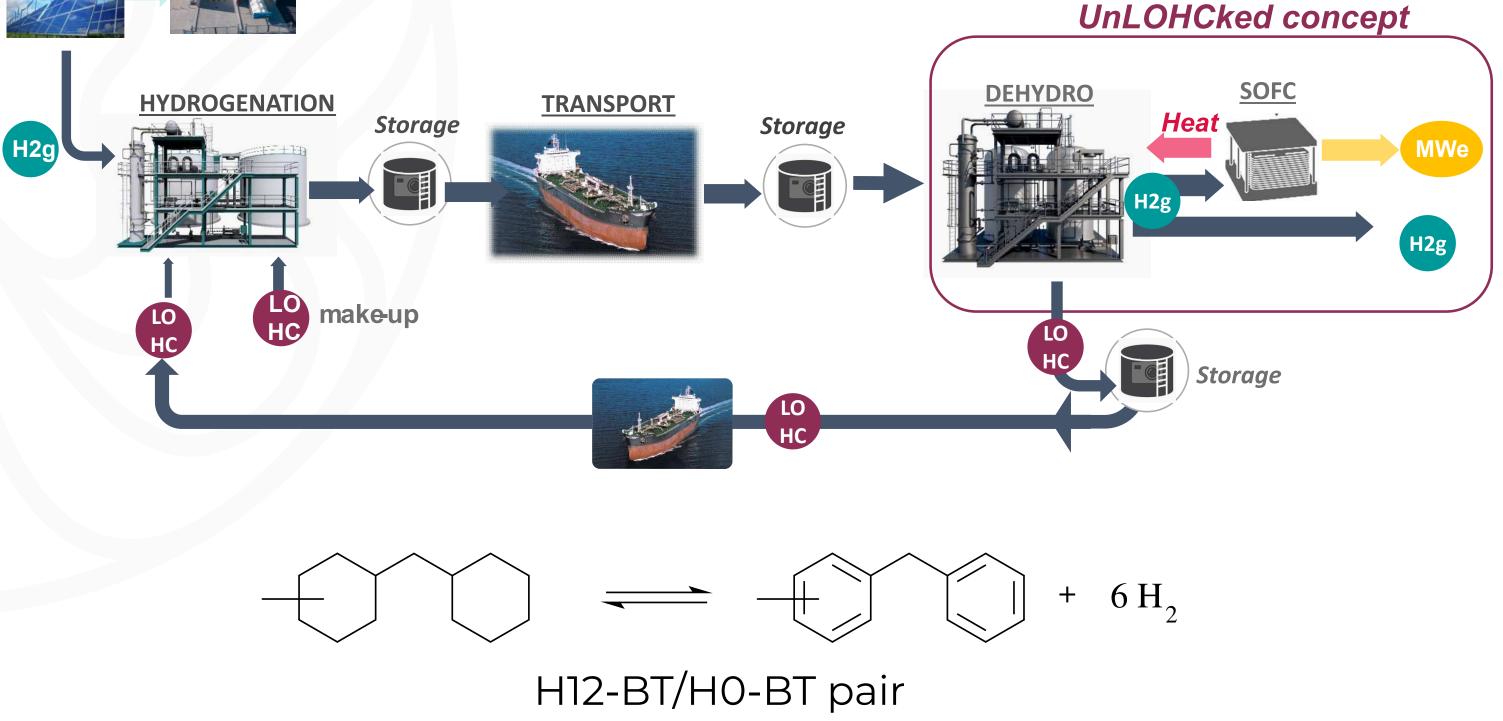
Context of LOHC

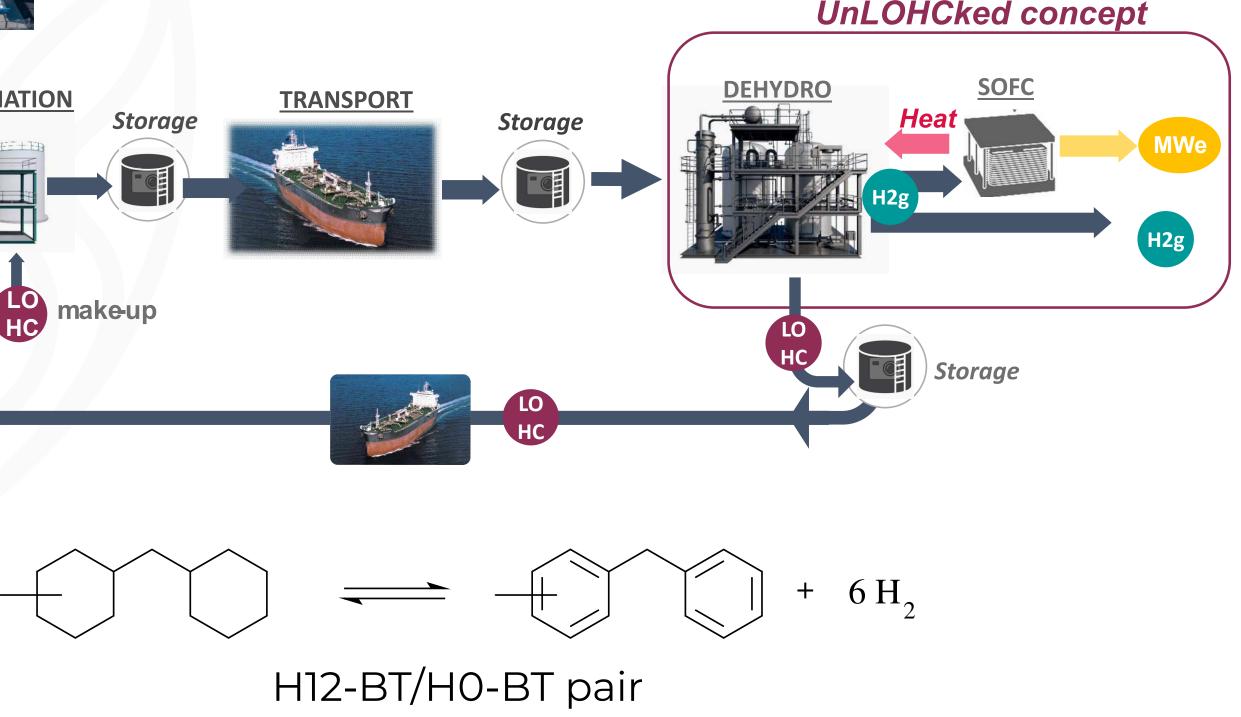
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RE & DRODUCTION









Methodology

REACTOR DESIGN Context of LOHC & MANUFACTURE The project **EXPECTED** Methodology **OUTCOMES** Tasks **Conversion >95%;** Dehydrogenation improved thermal issues efficiency; cost effective Dehydrogenation SYSTEM & ease of operation; reactor VALIDATION integrated systems Liquid phase analysis HO-BT/H12-BT pair CATALYST **Testing and** Catalysts **DEVELOPMENT** evaluation in 0 Bimetallic catalysts stationary unit Single-atom catalysts... **Development of low/free** ...or nano-clusters **CRM catalyst for LOHC** Hsp supports for Modelling activities dehydrogenation at lower hydrogenation Thermal coupling for the temperature Hsp supports for system integration: Batch & dehydrogenation dehyd reactor & SOFC continuous Conclusion testing ICC 2024 **Novel catalysts with metallic/bimetallic** structures TRL3 **CRM-free or low CRM content Novel preparation processes in order to**

 Novel preparation processes in order increase metal dispersion in an engineered support





Demo system, running for ≥500 hours and producing ≥10 kg H2/day at atmospheric pressure



Scalability of the developed system to largescale production for long distance transportation





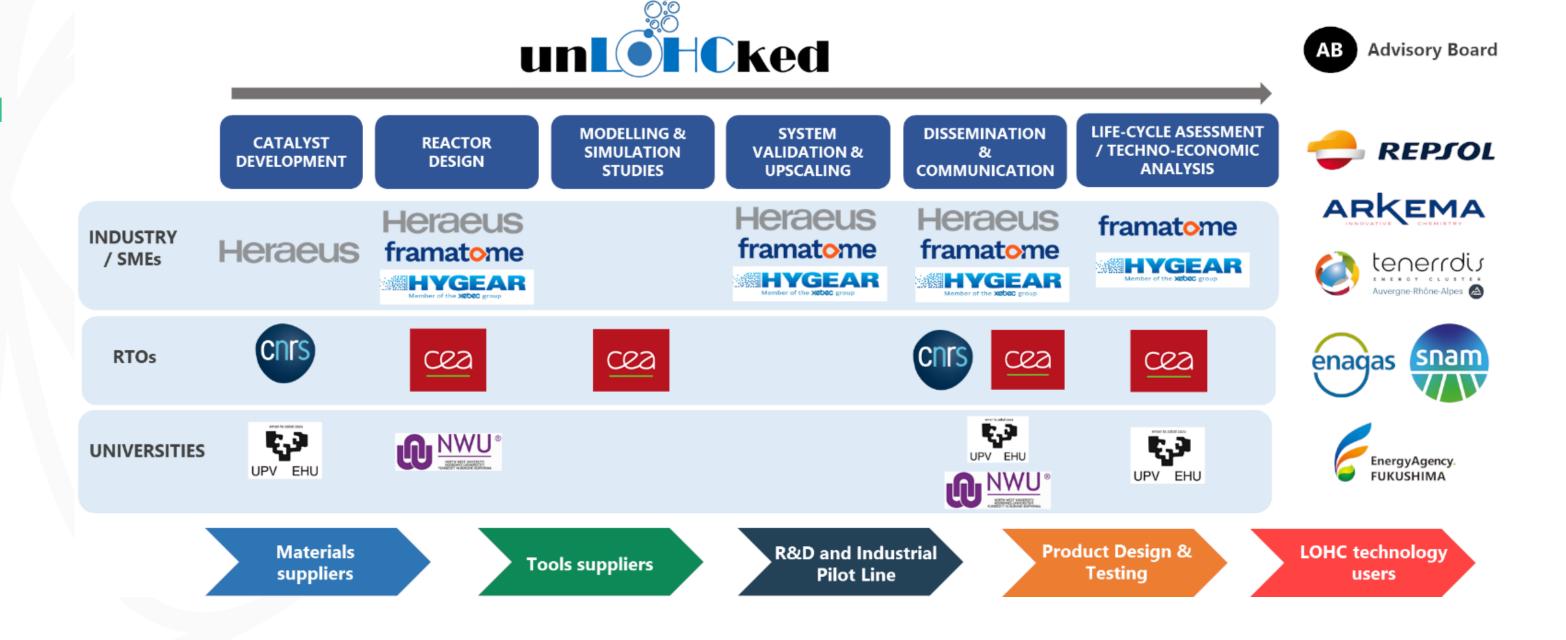
 Life-cycle assessment (LCA) for the whole supply chain
Techno-economic analysis (TEA) for 100-1,000 t H2/day system

CO2-free dehyd system integrated: SOFC & LOHC operating

ACTIVITIES & CHALLENGES

Tasks

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Dehydrogenation issues

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- Only PGM catalysts are highly active and selective •
- The dehydrogenation enthalpy is high and the reaction must be per-• formed at high T°C (250-300°C)
- Some by-products of the reaction (traces) avoid the complete cycling • dehydrogenation/hydrogenation
- Some catalyst deactivation may occur



Dehydrogenation reactor

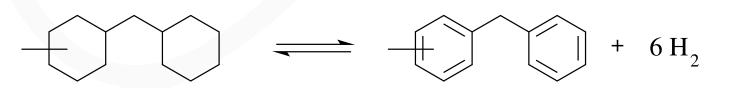
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Test in stirred reactors (G/L/S) with continuous removal of hydrogen (H_2 flow rate measurement).

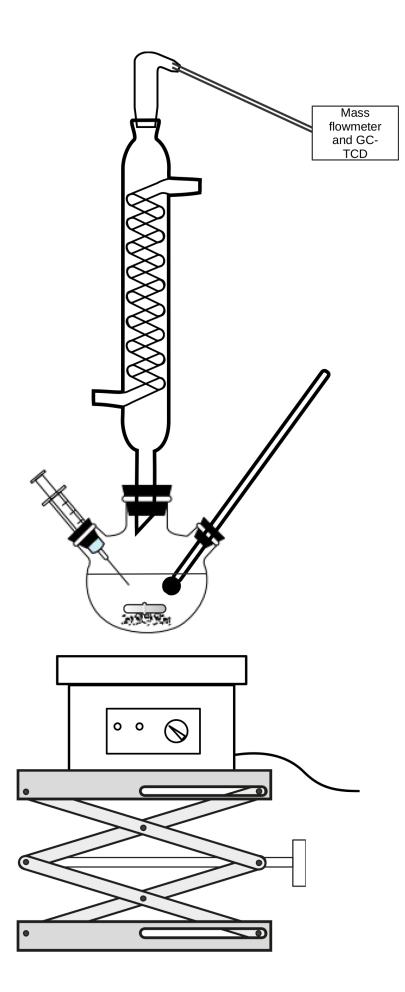
Different temperatures

Different catalyst loadings

No solvent







Liquid phase analysis

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Liquid phase analysis

HO-BT/H12-BT pair Catalysts Bimetallic catalysts Single-atom catalysts... ...or nano-clusters Hsp supports for hydrogenation Hsp supports for dehydrogenation Conclusion ICC 2024

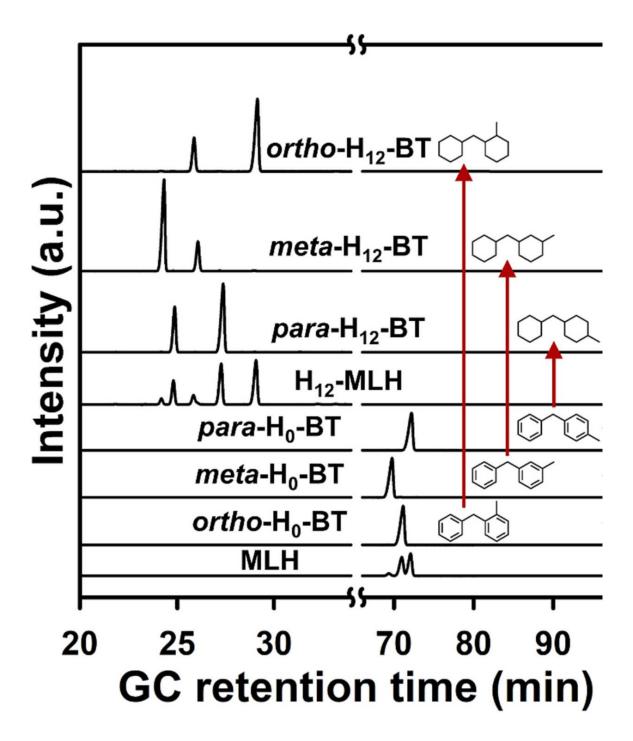
Analysis of LOHC+ and LOHCmolecules by GC BUT many isomers at each dehydrogenation degree.

Known by-product: methyl-fluorene

+6H₂ para-H₁₂-BT para-H₀-BT



Kim, T. et al. Journal of Energy Storage, 2023, 60, 106676



HO-BT/H12-BT pair

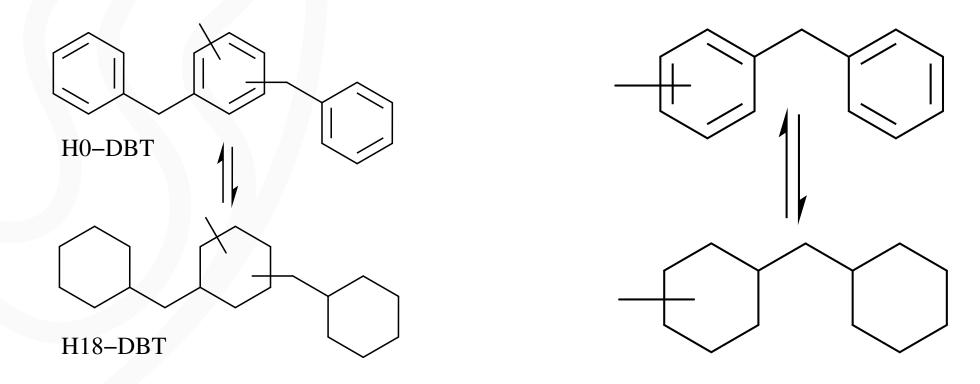
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HO-BT/H12-BT pair

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Few developments dedicated to Benzyltoluene/H12-BT.

System much less studied than HO-DBT/H18-DBT, should be less complex.



- High volumetric storage density (54.5 kgH₂/m³ at RT) Liquid in a large range of T°C (-70 to +270°C) Excellent robustness in hydrogenation/dehydrogenation cycles

- Low viscosity for easy handling
- Reaction rates (Hyd/Dehyd) higher compared to those of the DBT-• based LOHC system (same conditions).

T. Rüde et al. Sustainable Energy Fuels, 2022, 6, 1541-1553

Catalysts

Context of LOHC The project

- Methodology
- Tasks
- Dehydrogenation issues Dehydrogenation reactor

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HO-BT/H12-BT pair

Catalysts

Bimetallic catalysts Single-atom catalysts... ...or nano-clusters Hsp supports for hydrogenation Hsp supports for dehydrogenation Conclusion ICC 2024

Some ideas in the literature:

- WOx-incorporated Pt/Al₂O₃ > Pt/Al₂O₃ (H18-DBT) C. H. Kim et al. Fuel, 2022, 313, 122654
- Ni-modified catalysts active (MCH) ulletY. K. Gulyaeva et al. Cataysts, 2020, 10, 1198

Strategy followed for the UnLOHCked project: Develop bimetallic catalysts (NiZn, NiCu, NiSn but also PtSn, PtNi)

- Develop single-atoms catalysts
- Develop hydrogen spillover (Hsp) zeolites
- Re, Fe, Mo, Zr mono and bimetallic catalysts (with Pt). Conventional preparation (IWI) and ScCO₂ preparation





Bimetallic catalysts

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Single-atom catalysts... ...or nano-clusters Hsp supports for hydrogenation Hsp supports for dehydrogenation Conclusion ICC 2024 NiCu and NiZn known to selectively dehydrogenate methylcyclohexane. 2nd metal allows an increase of selectivity compared to Ni alone.



Bimetallic catalysts

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Bimetallic catalysts

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Stategy:

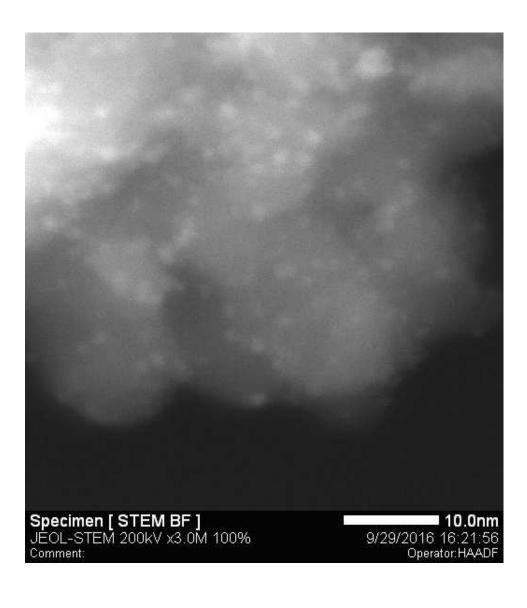
- co-impregnation
- 2-steps SOMC chemistry
- Preparation of Ni silicide NPs in solution further immobilised onto supports
- => different sizes (from 1.5 to 20-50 nm) and different alloy phases.

NiZn: Al-ShaikhAli, A. H. et al. Chem. Commun., 2015, 51, 12931-12934 NiCu: Gulyaeva, Y. K. et al. Catalysts, 2020, 10, 1198 SOMC: Docherty, S. R. et al. JACS Au, 2021, 1, 450-458 Ni NPs: Galeandro-Diamant, T. et al. Catal. Sci. Technol., 2019, 9, 1555 - 1558



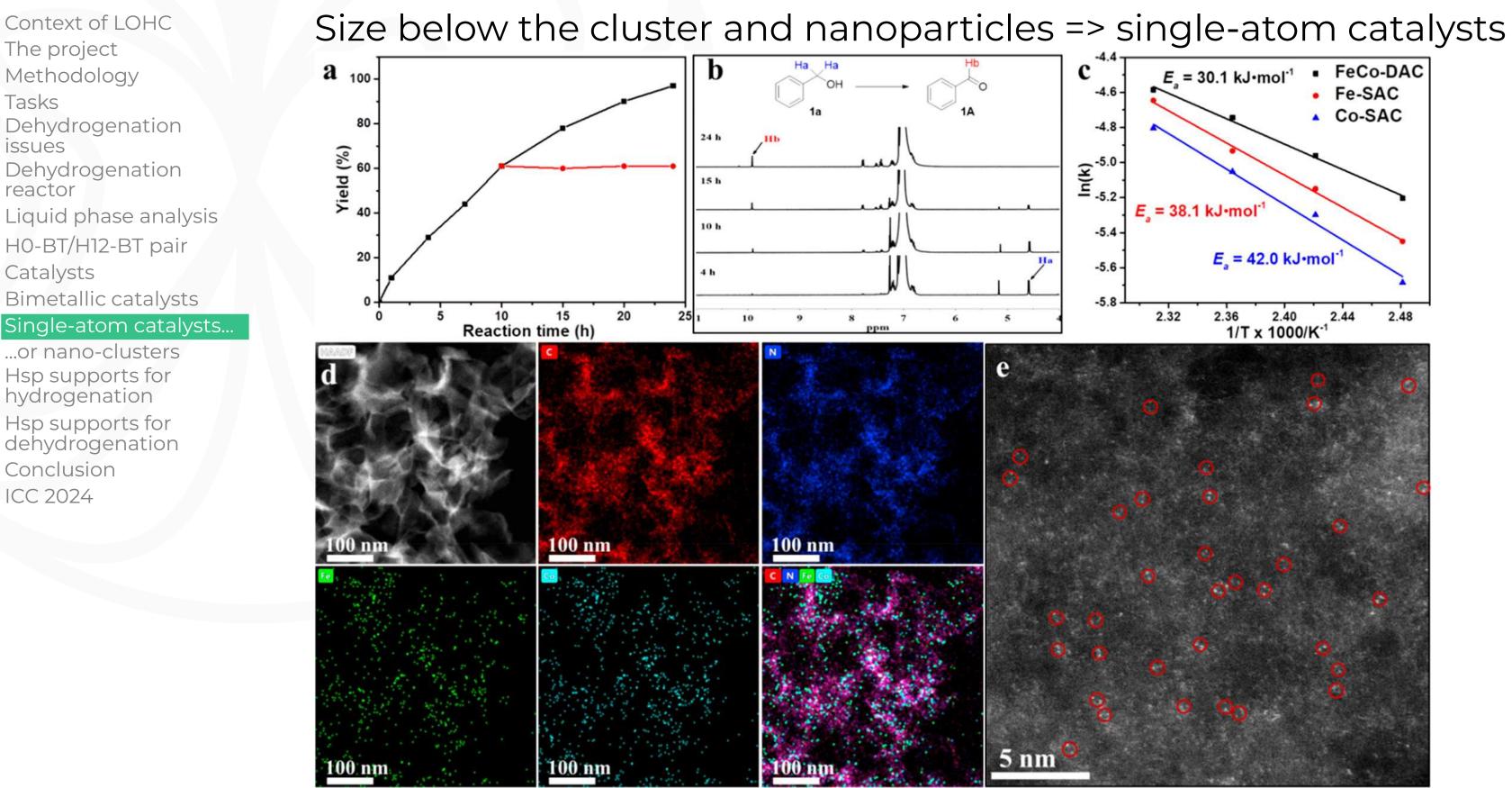


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STEM-HAADF of Ni/SiO₂

Single-atom catalysts...



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Hsp supports for hydrogenation Hsp supports for dehydrogenation Conclusion ICC 2024



Ircelyon ^{Liu, C.} et al, JACS, 2022, 144, 4913-4924

...or nano-clusters

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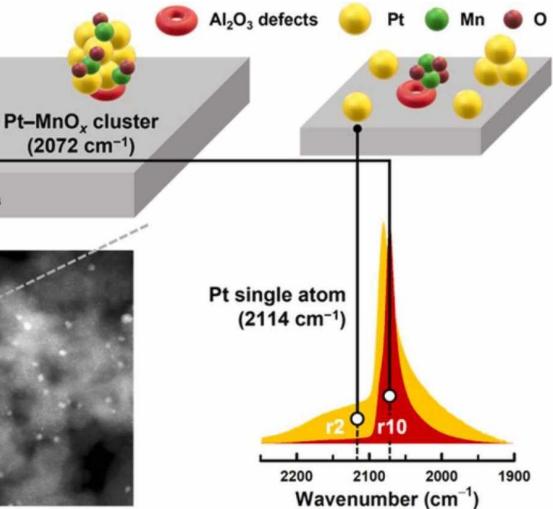
Ramp rate in H₂ reduction (°C min⁻¹) 10 Mesoporous Al₂O₃ H₁₂-BT → H₂ 56 DoDH (mol%) (r2) (r5) 83 (r10) H₀-BT

Mesoporous Pt-0.33MnO_x-Al₂O₃ (mPt0.33MnA)

- The higher ramp rate in H_2 reduction of mPtMnA leads to activity ulletimprovement.
- Pt nanoclustering with MnOx (< 2 nm) favored

Jo, Y. et al, Appl. Catal. B, 2023, 334, 122848





Hsp supports for hydrogenation

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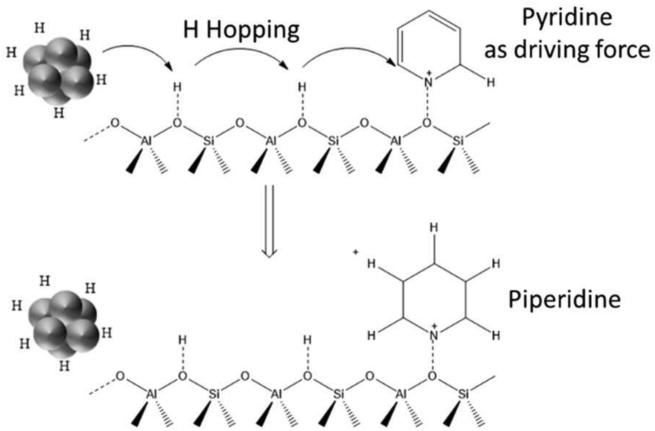
Hsp supports for dehydrogenation Conclusion ICC 2024

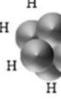
MFI and CHA, supporting metal nanoclusters (size < 2 nm) Hydrogen spillover phenomenon to enhance the active phase.

Compromise between H₂ diffusion and H spillover => modification of the standard zeolite properties:

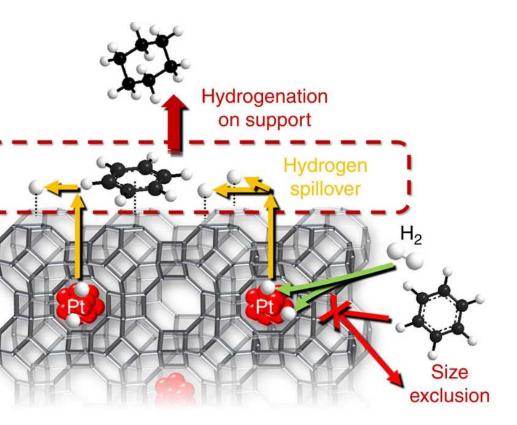
- Brønsted acidity ullet
- Si/Al ratio
- Extra framework aluminum
- Si-OH

Batalha, N. et al. Catal. Sci. Technol. 2022, 12, 1117-1129 Im, J. et al. Nature Communications, 2014, 5,3370









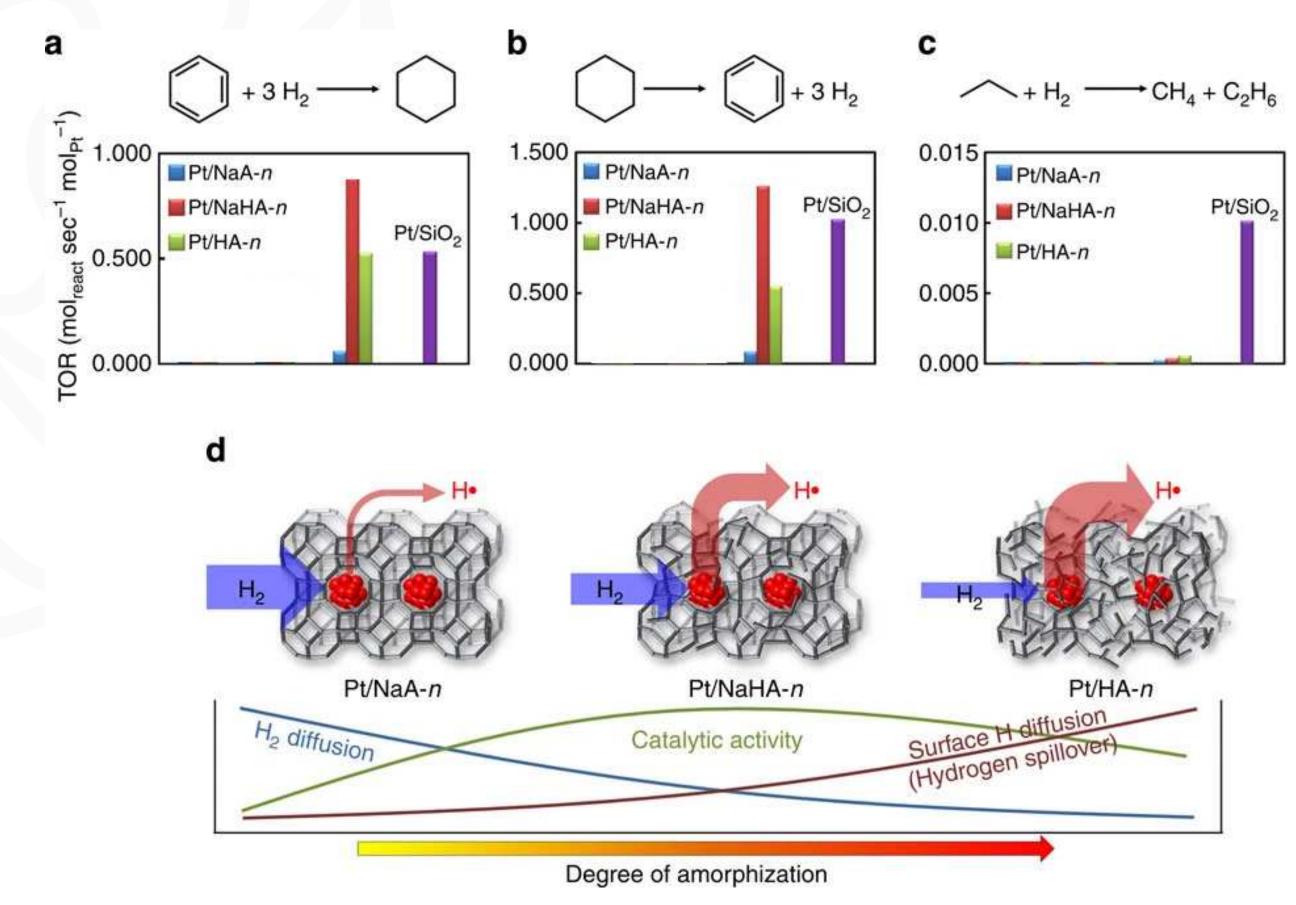
Hsp supports for dehydrogenation

Dehydrogenation enhanced by reverse hydrogen spillover

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Conclusion

ICC 2024

- UnLOHCked kick-off meeting on July
- Catalyst development from July 2023 to July 2025
- Upscaling of the best catalyst(s) by Heraeus
- Coupling with SOFC
- Demo end 2026



/ 5 to July 2025 eraeus

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Thanks to:

- Antoinette Boréave
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- Guillaume Fabre
- Franck Morfin
- Laurent Veyre



THANKS FOR YOUR ATTENTION



/ to July 2025 eraeus



European Commission

ICC 2024

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ICC 2024



Short-symposium "Catalytic reactions for hydrogen storage and release" (R. Janot, N. Bion, V. Meille...).

- LOHC
- Circular storage (NH₃)
- Solid-state H₂ storage: Catalytic reactions to enhance the dehydrogenation

PARTICIPATE TO ICC 2024 in LYON!

